OFFICE OF NAVAL RESEARCH

Research Contract N00014-90-J-1178

R&T Code 413r008---001

Principal Investigator: **R. Stanley Williams**

Organization: **Regents of the University of California**

TECHNICAL REPORT No. 3

SOLID-PHASE EQUILIBRIA FOR METAL-SILICON-OXYGEN TERNARY SYSTEMS

I: Mg, Ca, Sr AND Ba

by

H. Yuan and R.S. Williams

(in preparation)

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
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Distribution/

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A-1

University of California, Los Angeles
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Los Angeles, CA 90024-1569

July 1, 1990

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	**1b RESTRICTIVE MARKINGS** N/A
2a. SECURITY CLASSIFICATION AUTHORITY N/A	**3. DISTRIBUTION/AVAILABILITY OF REPORT** Approved for public release; distribution unlimited
2b DECLASSIFICATION/DOWNGRADING SCHEDULE N/A	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) N/A	**5. MONITORING ORGANIZATION REPORT NUMBER(S)**

6a NAME OF PERFORMING ORGANIZATION The Regents of the University of Californi	**6b OFFICE SYMBOL** *(If applicable)*	**7a NAME OF MONITORING ORGANIZATION** 1) ONR Pasadena - Administrative 2) ONR Alexandria - Technical
6c. ADDRESS (City, State, and ZIP Code) Office of Contracts & Grant Administration U C L A, 405 Hilgard Avenue Los Angeles, CA 90024		**7b. ADDRESS (City, State, and ZIP Code)** 1) 1030 E. Green Street, Pasadena, CA 91106 2) 800 N. Quincy St., Arlington, VA 22217-500

8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	**8b OFFICE SYMBOL** *(If applicable)* ONR	**9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER** N00014- 90-J-1178

8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street, 614A:DHP Arlington, VA 22217-5000	**10 SOURCE OF FUNDING NUMBERS**			
	PROGRAM ELEMENT NO.	**PROJECT NO.**	**TASK NO.**	**WORK UNIT ACCESSION NO**

11. TITLE (Include Security Classification)

UNCLASSIFIED: Solid phase equilibria from metal-silicon-oxygen ternary systems: I - Mg, Ca, Sr and Ba

12 PERSONAL AUTHOR(S)
Haojie Yuan and R.S. WILLIAMS

13a. TYPE OF REPORT Tech Rept #3	**13b TIME COVERED** FROM 10/1/89 TO 5/31/90	**14. DATE OF REPORT (Year, Month, Day)** 29 June 1990	**15. PAGE COUNT** 14 + 4 figs

16. SUPPLEMENTARY NOTATION

17.	COSATI CODES		**18 SUBJECT TERMS** (Continue on reverse if necessary and identify by block number)
FIELD	**GROUP**	**SUB-GROUP**	ternary phase diagrams; explanation of experimental results
			thin-film chemical reactions; design of stable compound
			structures chemical stability at interfaces.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Ternary phase diagrams for systems of the type M-Si-O, where M = Mg, Ca, Sr, and Ba, have been derived. These phase diagrams can be used to understand experimental results reported in the literature for thin film chemical reactions of SrO on Si and provide guides in designing stable structures that involve different materials in intimate contact. These particular phase diagrams are especially relevant for investigating the chemical stability of interfaces between SiO_2 and the oxide superconductors.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	**21. ABSTRACT SECURITY CLASSIFICATION** UNCLASSIFIED
22a NAME OF RESPONSIBLE INDIVIDUAL R. Stanley Williams	**22b TELEPHONE (Include Area Code)** (213) 825-8818 **22c OFFICE SYMBOL** UCLA

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted. SECURITY CLASSIFICATION OF THIS PAGE
All other editions are obsolete.

Solid phase equilibria for metal-silicon-oxygen ternary systems I: Mg, Ca, Sr and Ba

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Abstract

Ternary phase diagrams for systems of the type M-Si-O, where M=Mg, Ca, Sr and Ba, have been derived. These phase diagrams can be used to understand experimental results reported in the literature for thin film chemical reactions of SrO on Si and provide guides in designing stable structures that involve different materials in intimate contact. These particular phase diagrams are especially relevant for investigating the chemical stability of interfaces between SiO_2 and the oxide superconductors.

I. Introduction

Chemical reactions that occur at the interfaces separating different solids are scientifically interesting and technologically important. Many studies have shown that one of the first steps in understanding and controlling interfacial chemistry is to map the

bulk phase diagram containing the elements of interest.[1-6] These phase diagrams can be used to predict the occurrence of reaction products, or, conversely the stability of the phases present at the interfaces between different materials. Hence, bulk phase diagrams can provide guides in designing thin film structures and in selecting candidate materials to form chemically stable interfaces.

In this work, we derived phase diagrams for systems of the type M-Si-O, where M=Mg, Ca, Sr and Ba. These phase diagrams are important for understanding how elemental Si interacts with the Group II metal oxides (MgO, CaO, SrO and BaO), how the Group II metals interact with SiO_2, and how the oxide superconductors interact with SiO_2 and Si. We will describe how to determine such phase diagrams, present the ternary diagrams for the M-Si-O systems, and discuss the use of these phase diagrams for understanding interfacial chemistry.

II. Determination of Ternary Phase Diagrams

The procedures required for mapping out ternary phase diagrams have been discussed in detail by several authors.[2,4,5] The convention in this paper follows that established by Thurmond et al.[2] for representing the solidus portion of a ternary diagram involving oxygen as one of the components; the partial pressure of oxygen in the system is chosen to be 1atm. Isothermal sections of the diagrams are represented as equilateral triangles with each apex representing a system containing only a single element, in this case oxygen, silicon or a Group II metal. The sides of the triangle present

the compounds that can exist in each of the possible binary systems. The interior of the diagram is subdivided by tie lines into smaller triangles that represent the regions of three phase equilibrium. The tie-lines can be determined by simple calculations if the Gibbs free energy of formation (ΔG_f) of all the phases in the systems are known.

Unfortunately, the thermochemical data base has large gaps and many uncertainties, so in practice, phase diagrams have been constructed with the use of several approximations supplemented by experimental determinations of phase stability.[1-6] The major assumption often made is that the entropic contribution to a solid state reaction is negligible and that the phase stabilities may be determined from the enthalpies of formation (ΔH_f). Another assumption used here is that the phases have a negligible solid solubility in one another, so that the tie lines are straight and phase boundaries are abrupt. Finally, if no ΔH_f data exist for a particular phase, it can be estimated by interpolation procedures from known phases. For this work, the missing data were estimated using the method in Ref. 7.

For the case of the M-Si-O systems studied here, many references have been consulted to find what phases exist in each ternary system.[8-16] There have been several determinations and updates of most of the ΔH_f data required to estimate the phase diagrams.[8-13] The ΔH_f data obtained from Refs. 8 to 13 were compared and it was found that the agreement among the different references for which duplication occurs is very good. The only phases for which no data at all were found were three of the barium

silicates and $BaSi_2$ (Table IV), and these data were estimated.[7] Since the data in Refs. 8 and 9 were included in Ref. 11 and the data in Ref. 11 were more up-to-date, these data are presented in the tables. The tables also contain data from Refs. 10, 12 and 13 as well as the estimated data, although whenever possible the data from Ref. 11 were used in the calculations to ensure consistency among the values.

The calculated enthalpy change for a reaction used in determining the position of a tie-line in a phase diagram is subject to the following uncertainties: (1) the phase diagrams are for the standard states at 298K and 1atm, but the data from Ref. 11 are for the conditions of 298K and 0.1MPa. According to Ref. 11, this minor difference in pressure will not affect the tabulated data for the solid compounds. (2) The data from Ref. 11 are characterized by absolute experimental uncertainties of less than 8kJ, with the relative uncertainties considerably smaller. The uncertainties are 13kJ for Ca_2Si and 8kJ for Ca3i and $CaSi_2$ according to Ref. 10. (3) The data from the other references, which do not have uncertainties listed, and the estimated data are assumed to have uncertainties comparable to the largest values for the tabulated phases.

In the Mg-Si-O system, all the data used for the calculations were taken from Ref. 11. The magnitude of the enthalpy changes for all the reactions used for determining the phase diagram in Fig. 1 was more than 150kJ, which is larger than the worst-case estimated uncertainty calculated for any of the reactions. In the Ca-Si-O system shown in Fig. 2, the magnitude of the enthalpy changes for all the reactions are reasonably greater than the worst-

case estimated uncertainties for these reactions except for the following reaction:

$$4CaO + 3CaSi_2 \Rightarrow Ca_2SiO_4 + 5CaSi, \qquad \Delta H = -74kJ, \qquad (1)$$

which has a smaller enthalpy change than the worst-case estimated uncertainty for this reaction which is 107kJ. Therefore, we used a dashed line in Fig. 2 to connect Ca_2SiO_4 and CaSi to indicate the uncertainties of this tie line. In the Sr-Si-O system in Fig. 3, four compounds have ΔHf values obtained from references other than Ref. 11, and there are no estimated uncertainties for these values. Because nearly all the calculated reaction enthalpies had magnitudes larger than 130kJ, all but one of the tie-lines are certainly correct. The one possible exception is for the reaction:

$$3SiO_2 + 5SrSi \Rightarrow 2SrSiO_3 + 3SrSi_2, \qquad \Delta H = -28kJ. \qquad (2)$$

Thus, the tie-line connecting $SrSiO_3$ to $SrSi_2$ is uncertain because ΔH for reaction (1) is relatively small, so it is shown as a dashed line in the figure. In the Ba-Si-O system of Fig. 4, the enthalpy changes for all the reactions are more than 170kJ and most of the values are more than 500kJ. Therefore, the uncertainties related to the tabulated data obtained from the references are negligibly small for the tie line determination, but there are possible uncertainties with tie-lines involving the compounds $BaSi_2$, Ba_3SiO_5, $Ba_5Si_8O_{21}$ and $Ba_3Si_5O_{13}$, since the enthalpy data for these compounds were estimated.

The phase diagrams presented in Figs. 1-4 were determined from the data tabulated in Tables I-IV, respectively, and calculations of all possible binary tie-line crossings. These phase diagrams were calculated from ΔH_f data at 298K, but since the temperature dependence of the enthalpies is weak and should be roughly similar for all the oxide phases, the diagrams are probably correct over a range from 0K to nearly the temperature of the lowest melting eutectic in each system.

III. Discussion

The primary feature shared by all the diagrams in Figs. 1-4 is that a series of ternary compounds, i. e. metal silicates, are intermediate in composition between the metal monoxide and silicon dioxide. These M-Si-O phase diagrams can be classified according to how elemental Si interacts with the various oxides:

(1) the metal monoxide and all the metal silicates are connected to Si by a tie line (Mg-Si-O),

(2) the metal monoxide is not connected to Si but several metal silicates are (Ca-Si-O) and

(3) no tie lines connect Si to the metal monoxide or any metal silicate (Sr-Si-O and Ba-Si-O).

Thus, elemental Si cannot reduce MgO or Mg silicates, whereas an excess of Si can reduce any of the oxides or silicates of both Sr and Ba to their respective disilicides. An intermediate situation exists for the Ca oxides and silicates, in which excess Si can react with CaO or Ca_3SiO_5 to form $CaSi_2$ and Ca_2SiO_4, but does not react

with Ca_2SiO_4, $Ca_3Si_2O_7$ or $CaSiO_3$. On the other hand, in all cases excess elemental Group II metals can reduce SiO_2 and all the silicates to silicides.

This type of information is extremely valuable if one wishes to evaluate the possibility of using different oxides as insulating layers on Si as alternatives to SiO_2. For example, Kado and Arita[17] reported on the growth of SrO films on Si. This system is of interest because SrO has a cubic crystal structure and is nearly lattice matched to Si. Thus, there was an intriguing possibility for growing heteroepitaxial structures. However, when Himpsel et al.[18] examined this system using photoemission, they found that SrO reacted with Si during the deposition to form Sr silicates. This observation is in agreement with the phase diagram in Fig. 3, which furthermore predicts that Sr silicides should also have been formed in the reaction of SrO with Si. The actual products formed and their distribution on the Si substrate depends on the deposition and growth conditions (i. e. kinetic parameters), but if the system had been heated long enough to reach equilibrium, the deposited and reacted film would consist of a mixture of SiO_2 and $SrSi_2$. Such films are clearly not desirable insulators since the silicide is metallic, and thus if these phase diagrams had been available at the time, the experiments reported in Ref. 18 would not have been necessary.

Taking the opposite approach, one can examine the phase diagrams to determine what other oxides involving Group II metals are chemically stable with respect to Si. The list is not long: MgO, Mg_2SiO_4, $MgSiO_3$, Ca_2SiO_4, $Ca_3Si_2O_7$ and $CaSiO_3$. Whether any of these

phases would be of interest as insulators on Si depends on their structural and electrical properties, and significant amounts of research would be required to grow such films and evaluate their properties.

The phase diagrams in Figs. 2-4 can also be used to estimate whether or not various forms of the new oxide superconductors are compatible with Si or SiO_2. Williams and Chaudhury[19] have analyzed the thermodynamic stability of the $YBa_2Cu_3O_7$ (YBCO) phase with respect to other materials, and found that a good approximation of ΔH_f for YBCO is simply the sum of ΔH_f's for the component oxides. Both Si and SiO_2 react with YBCO to form more stable products, predominantly Ba silicates. However, they demonstrated that YBCO does not react with $BaSi_2O_5$, because of the extreme thermochemical stability of this compound.[19] Based on this information and the phase diagrams presented here, both Si and SiO_2 can also be ruled out as suitable substrates for either Ca- or Sr- containing oxide superconductors, but various silicates may prove to be suitable as chemically inert substrates.

Several ternary oxides, such as $SrTiO_3$, $LaAlO_3$ and $LaGaO_3$, have been used with considerable success as substrates for growing highly oriented YBCO films.[20,21,22] These materials provide a good lattice match for the (001) surface of YBCO, and they appear to be chemically inert. This is most likely because these ternary oxides are also thermochemically very stable. An examination of the crystal structures of the group II metal silicates reveals that one high temperature phase of Ca_2SiO_4 is orthorombic with lattice constants a=5.46Å and c=7.19Å.[23] If this phase can be stabilized, it

could also prove to be a reasonable substrate for YBCO. This material and other silicates are the subject of continuing investigations.

The major caveat to remember when applying these phase diagrams to real thin film systems is that they are strictly valid only for closed systems with one atmosphere of oxygen gas present. For systems that are examined in vacuum or utilized in ambient conditions, gas phase species such as SiO that may form on heating can escape and thus change the composition of a film from its as-deposited stoichiometry.[6] With this in mind, the ternary phase diagrams provided here should prove to be very useful for designing thin film systems that incorporate the Group II metals, silicon and oxygen.

IV. Summary

Ternary phase diagrams have been determined for the M-Si-O systems, where M = Mg, Ca, Sr and Ba. These phase diagrams can be used to explain previous experimental results for reactions between SrO films on Si and to predict what can happen at the interfaces between M-containing compounds and either Si or SiO_2. These phase diagrams are not difficult to determine, yet they are important in providing guides in designing experiments and in selecting chemically stable materials for thin film structures.

Acknowledgments

Table I: Enthalpies of formation (kJ/mol) of the phases
in the Mg-Si-O system at 298K and 1atm

==

	Ref. 11
SiO_2	-910.94 (α quartz)
	-909.48 (α cristobalite)
	-909.06 (α tridymite)
	-903.5 (amo.)
MgO	-601.70
	-597.98 (micro)
Mg_2Si	-77.8
Mg_2SiO_4	-2174.0
$MgSiO_3$	-1549.00

==

Table II: Enthalpies of formation (kJ/mol) of the phases
in the Ca-Si-O system at 298K and 1atm

	Ref. 10	Ref.11
SiO_2*		
CaO		-635.09
CaO_2		-652.7
Ca_2Si	-209	
CaSi	-151	
$CaSi_2$	-151	
Ca_3SiO_5		-2929.2
Ca_2SiO_4		-2307.5 (β)
		-2317.9 (γ)
$Ca_3Si_2O_7$		-3961.0
$CaSiO_3$		-1634.94 (wollastonite)
		-1628.4 (pseudowollastonite)

* Data for SiO_2 are the same as those in Table I.

Table III: Enthalpies of formation (kJ/mol) of the phases
in the Sr-Si-O system at 298K and 1atm

	Ref. 10	Ref. 11	Ref. 12	Ref. 13
SiO_2*				
Sr_2O		-647.3		
SrO		-592.0		
SrO_2		-633.5		
Sr_2Si				-398.2
SrSi	-472			
$SrSi_2$	-616.1			
Sr_3SiO_5			-2792.2	
Sr_2SiO_4		-2304.5		
$SrSiO_3$		-1633.9		

* Data for SiO_2 are the same as those in Table I.

Table IV: Enthalpies of formation (kJ/mol) of the phases
in the Ba-Si-O system at 298K and 1atm

	Ref. 10	Ref. 11	Ref. 12	estimated
SiO_2*				
Ba_2O		-615.5		
BaO		-553.5		
BaO_2		-634.3		
$BaSi$	-757			
$BaSi_2$				-1229
Ba_4SiO_6			-3249.1	
Ba_3SiO_5				-2827
Ba_2SiO_4		-2287.8		
$BaSiO_3$		-1623.60		
		-1573 (amo.)		
$Ba_2Si_3O_8$		-4184.8		
$Ba_5Si_8O_{21}$				-1872
$Ba_3Si_5O_{13}$				-1435
$BaSi_2O_5$		-2548.1		

* Data for SiO_2 are the same as those in Table I.

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Figure Captions

Fig. 1. Mg-Si-O phase diagram at 298K and 1atm. Compounds from left to right on the MgO-SiO$_2$ line are Mg$_2$SiO$_4$ and MgSiO$_3$.

Fig. 2. Ca-Si-O phase diagram at 298K and 1atm. Compounds from left to right on the CaO-SiO$_2$ line are: Ca$_3$SiO$_5$, Ca$_2$SiO$_4$, Ca$_3$Si$_2$O$_7$ and CaSiO$_3$.

Fig. 3. Sr-Si-O phase diagram at 298K and 1atm. Compounds from left to right on the SrO-SiO$_2$ line are Sr$_3$SiO$_5$, Sr$_2$SiO$_4$ and SrSiO$_3$. The dashed tie-line is somewhat uncertain as discussed in the text.

Fig. 4. Ba-Si-O phase diagram at 298K and 1atm. Compounds from left to right on the BaO-SiO$_2$ line are Ba$_4$SiO$_6$, Ba$_3$SiO$_5$, Ba$_2$SiO$_4$, BaSiO$_3$, Ba$_2$Si$_3$O$_8$, Ba$_5$Si$_8$O$_{21}$, Ba$_3$Si$_5$O$_{13}$ and BaSi$_2$O$_5$. Ba$_5$Si$_8$O$_{21}$ and Ba$_3$Si$_5$O$_{13}$ are not indicated on the diagram because their compositions are nearly indistinguishable from Ba$_2$Si$_3$O$_8$ and BaSi$_2$O$_5$. Both compounds are connected to BaSi$_2$ by tie-lines.
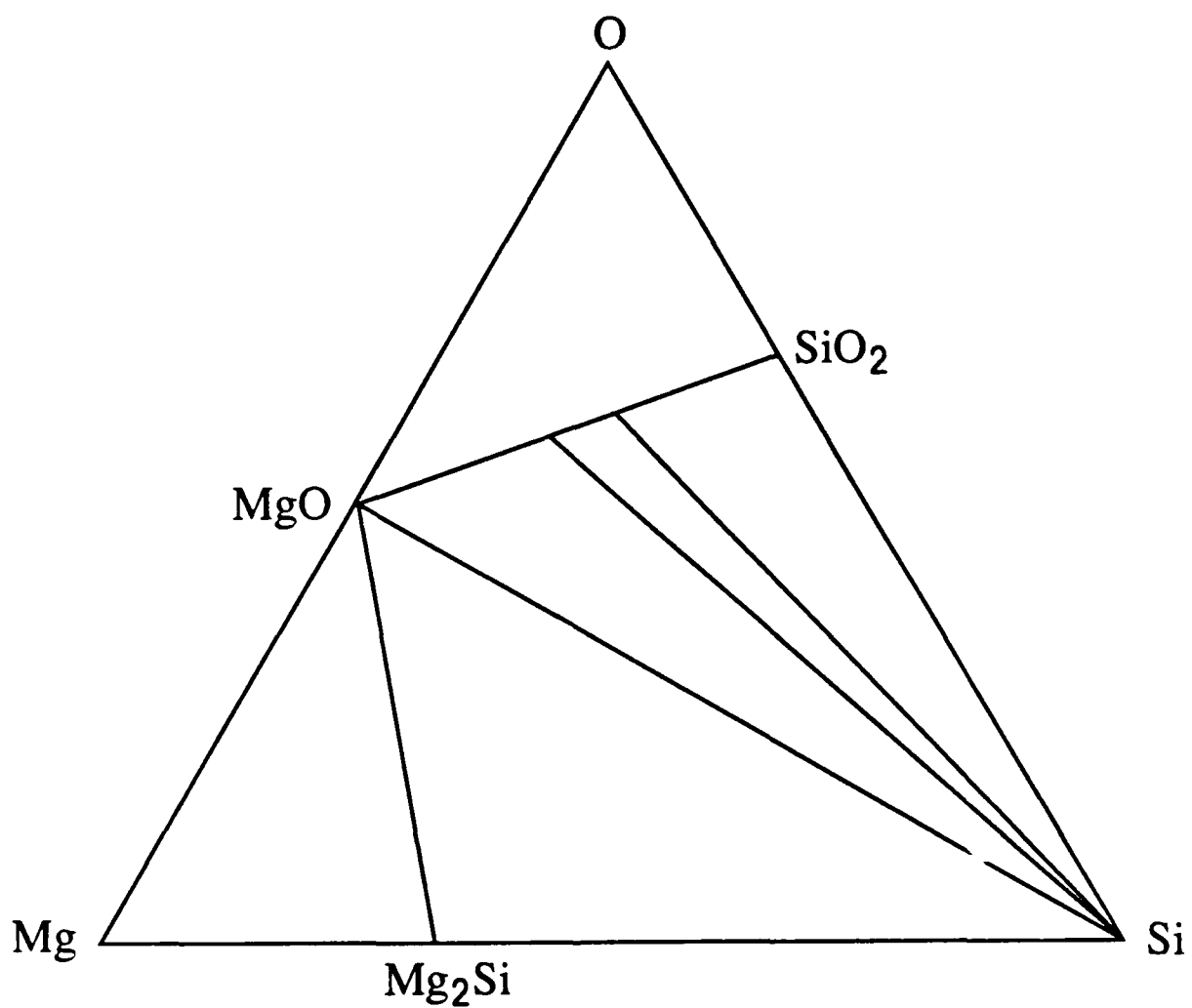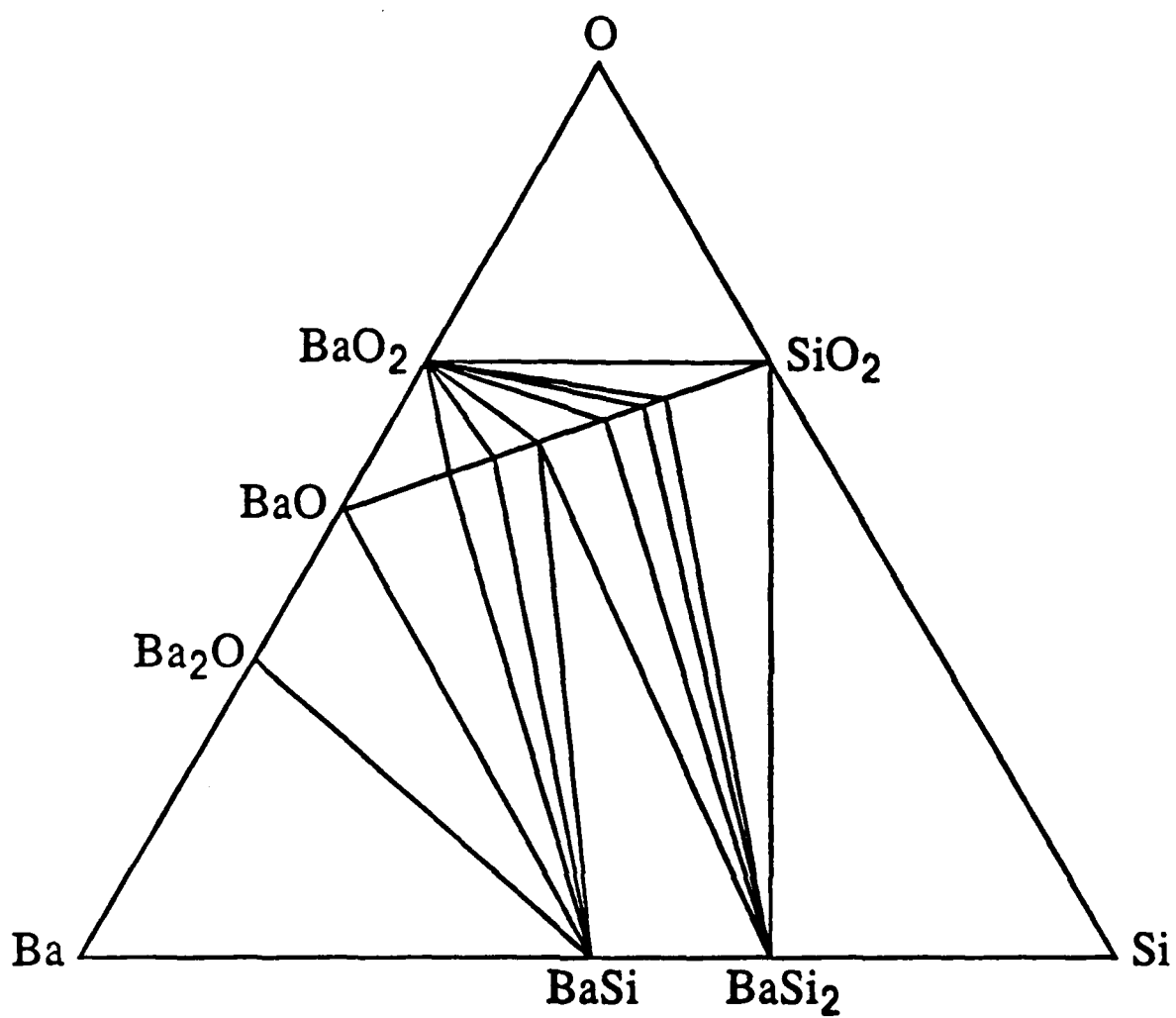
Fig. 1

Fig. 2

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Fig. 4